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Thermo-solutal modelling of microstructure formation during multiphase alloy solidification – a new approach

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Abstract. This paper shows how to move from a specification of free energy for the solidification of a binary alloy to the dynamical equations using the elegance of a dissipative bracket analogous to the Poisson bracket of Hamiltonian mechanics. A key new result is the derivation of the temperature equation for single-phase thermal-solutal models, which contains generalisations and extra terms which challenge standard models. We also present, for the first time, the temperature equation for thermal multi-phase field models. There are two main ingredients: one, the specification of the free energy in terms of the time and space dependent field variables: n -phases ϕ_i , a concentration variable c , and temperature T ; two, the specification of the dissipative bracket in terms of these variables, their gradients and a set of diffusion parameters, which may themselves depend on the field variables. The paper explains the method within this context and demonstrates its thermodynamic admissibility.

Introduction

The phenomena of alloy solidification as described and explained in for example, [1], is now routinely associated with the significant successes of the modelling methods of phase field. Although it is well known that dissipative phenomena at constant temperature and pressure spontaneously change to accommodate a lowering of the Gibbs free energy, the details of such transitions are still obscure for many complex materials. Current computing resources and methods still struggle to grapple with the highly non-linear partial differential equations the phase field method produces. Yet, in principle, the modelling of even complex materials using phase field is quite straightforward in outline: specify the free energy and allow the system to evolve spatially and temporally in such a way as minimise this functional in a thermodynamically consistent way. This manifests itself mathematically by the underlying presence of variational derivatives and diffusion parameters. To illustrate this, given a single phase formulation of the free energy, $F = \int_{\Omega} f(\phi, \nabla\phi, c, T) d^3x$, in a domain Ω for the thermal-solutal (T, c) solidification of a metal, where $\phi \in [0, 1]$ indicates bulk melt or bulk solid at the extremes, the dynamical equations are typically given in variational form for the phase variable [2]

$$\dot{\phi} = -M \frac{\delta F}{\delta \phi}, \quad (1)$$

a conserved variational form for the solute concentration variable

$$\dot{c} = \nabla \cdot D \nabla \left(\frac{\delta F}{\delta c} - \mathbf{j} \right) \quad (2)$$

and a temperature diffusion equation

$$C_p \dot{T} = \nabla \cdot \kappa \nabla T + L \dot{\phi}. \quad (3)$$

In the above M is phase mobility, D a solute diffusion parameter, C_p , κ and L are the volumetric heat capacity, thermal conductivity and volumetric latent heat parameters respectively- all prescribed. \mathbf{j} is an anti-trapping current that compensates for non-physical effects associated with the computationally

convenient use of a larger than realistic interface width. For this paper we will neglect \mathbf{j} , because it is not derived from a variational procedure. The presence of $\nabla\phi$ in the free energy indicates a penalty in the free energy, i.e. an increase, if the interface becomes too sharp. It is by no means obvious how three such different looking equations come from a single underlying principle. The form of these equations can be justified either by appeal to a sharp interface model [3] or thermodynamically [4].

This paper is concerned with the application of a generic non-equilibrium thermodynamic method to the formulation of a model for multiphase solidification. Such a model has been described without coupling to a temperature equation by [5] and although it might be perfectly feasible to start from this formulation using the methods of [4], we are here applying the generic methods of [6]– generic in the sense that these methods apply to any continuum system with or without dissipative behaviour. This method has more in common with [4] than [3], keeps the formal structure and the particular physical system concerned quite distinct and brings to light differences and clarification when compared with other models (including single phase models) in the literature.

The bracket formalism

The bracket formalism is a generalisation to both continuum and dissipative systems of the Poisson bracket of discrete particle systems. For an explanation of the methods, notation and generalised thermodynamic relations used in the following please see [6]. As is well known for conservative particle systems, dynamical equations are given once the Hamiltonian is prescribed in terms of the position and momentum. For example, a single particle of mass m in a potential well V the Hamiltonian energy is given in terms of the momentum, \mathbf{p} and position, \mathbf{x} by

$$H = \frac{1}{2} \frac{\mathbf{p} \cdot \mathbf{p}}{m} + V(\mathbf{x}), \quad (4)$$

giving the equations of motion

$$\dot{x}_i = \{x_i, H\}, \quad (5)$$

$$\dot{p}_i = \{p_i, H\}, \quad (6)$$

where the Poisson bracket is specified by the antisymmetric operator (for arbitrary variables A, B)

$$\{A, B\} \equiv \sum_i^3 \left(\frac{\partial A}{\partial x_i} \frac{\partial B}{\partial p_i} - \frac{\partial A}{\partial p_i} \frac{\partial B}{\partial x_i} \right). \quad (7)$$

This gives as expected

$$\dot{x}_i = \frac{p_i}{m}, \quad (8)$$

$$\dot{p}_i = -\frac{\partial V}{\partial x_i}, \quad (9)$$

but also, for example, because of antisymmetry

$$\dot{H} = \{H, H\} = 0, \quad (10)$$

the conservation of energy.

The dissipative bracket for two arbitrary *functionals*, A, B is denoted $[A, B]$ and the dynamical equations for a purely dissipative system with boundary at constant pressure and temperature are derived from

$$\dot{A} = [A, F], \quad (11)$$

where $F = E - ST$ is the Gibbs free energy functional, E is enthalpy, S is entropy and T is temperature. This notation is a little loose and, in terms of respective enthalpy and entropy densities e, s strictly means

$$F = \int_{\Omega} f d^3x = \int_{\Omega} (e - Ts) d^3x = E - \int_{\Omega} Ts d^3x. \quad (12)$$

The form of the dissipative bracket, in terms of enthalpy, E , for the single phase equations given above is

$$\begin{aligned} [A, E] = & - \int_{\Omega} M \frac{\delta A}{\delta \phi} \frac{\delta E}{\delta \phi} d^3x + \int_{\Omega} \frac{M}{T} \frac{\delta A}{\delta s} \frac{\delta E}{\delta \phi} \frac{\delta E}{\delta \phi} d^3x \\ & - \int_{\Omega} D \nabla \frac{\delta A}{\delta c} \cdot \nabla \frac{\delta E}{\delta c} d^3x + \int_{\Omega} \frac{D}{T} \frac{\delta A}{\delta s} \nabla \frac{\delta E}{\delta c} \cdot \nabla \frac{\delta E}{\delta c} d^3x, \\ & - \int_{\Omega} \frac{\kappa}{T} \nabla \frac{\delta A}{\delta s} \cdot \nabla \frac{\delta E}{\delta s} d^3x + \int_{\Omega} \frac{\kappa}{T^2} \frac{\delta A}{\delta s} \nabla \frac{\delta E}{\delta s} \cdot \nabla \frac{\delta E}{\delta s} d^3x, \end{aligned} \quad (13)$$

where Ω is the domain of the system. s is the entropy density, c the solute concentration and $T = T(\phi, c, s)$. The bracket is written in terms of enthalpy rather than Gibbs free energy so that we can more easily show that the flow of entropy density, s , is thermodynamically admissible. Together with the chain rule for functionals

$$\dot{A} = \int_{\Omega} \left(\frac{\delta A}{\delta \phi} \dot{\phi} + \frac{\delta A}{\delta c} \dot{c} + \frac{\delta A}{\delta s} \dot{s} \right) d^3x, \quad (14)$$

and the following generalised thermodynamic relation,

$$\left. \frac{\delta F}{\delta \phi} \right|_{c,T} = \left. \frac{\delta E}{\delta \phi} \right|_{c,s}, \quad (15)$$

which we shall write for convenience $\frac{\delta F}{\delta \phi} = \frac{\delta E}{\delta \phi}$, equations Eq.1 and Eq.2 are recovered (recall that $\mathbf{j} = \mathbf{0}$ and A is arbitrary). We also have

$$\dot{s} = \frac{M}{T} \frac{\delta E}{\delta \phi} \frac{\delta E}{\delta \phi} + \nabla \cdot \left(\frac{\kappa}{T} \nabla \frac{\delta E}{\delta s} \right) + \frac{\kappa}{T^2} \nabla \frac{\delta E}{\delta s} \cdot \nabla \frac{\delta E}{\delta s} + \frac{D}{T} \nabla \frac{\delta E}{\delta c} \cdot \nabla \frac{\delta E}{\delta c}. \quad (16)$$

To form an equation for T alone we require the generalised thermodynamic relations

$$T \equiv \left. \frac{\delta E}{\delta s} \right|_{c,\phi}, \quad s \equiv - \left. \frac{\delta F}{\delta T} \right|_{c,\phi}, \quad \left. \frac{\delta E}{\delta c} \right|_{\phi,s} = \left. \frac{\delta F}{\delta c} \right|_{\phi,T} \quad (17)$$

which together with Eq. 15 gives

$$\dot{s} = \frac{M}{T} \frac{\delta F}{\delta \phi} \frac{\delta F}{\delta \phi} + \nabla \cdot \left(\frac{\kappa}{T} \nabla T \right) + \frac{\kappa}{T^2} \nabla T \cdot \nabla T + \frac{D}{T} \nabla \frac{\delta F}{\delta c} \cdot \nabla \frac{\delta F}{\delta c}. \quad (18)$$

From Eq. 18, we see that there is a positive entropy source, σ and a flux, $\mathbf{J}_s = -\frac{\kappa}{T} \nabla T$, so that in differential form

$$\dot{s} + \nabla \cdot \mathbf{J}_s = \sigma \quad (19)$$

and the flow of s is seen to be thermodynamically admissible. On applying the chain rule for the density variables in terms of $\phi, \nabla \phi, c$ and T :

$$\frac{\partial}{\partial t} = \dot{\phi} \frac{\partial}{\partial \phi} + \nabla \dot{\phi} \cdot \frac{\partial}{\partial \nabla \phi} + \dot{c} \frac{\partial}{\partial c} + \dot{T} \frac{\partial}{\partial T} \quad (20)$$

to the left hand side of Eq. 18 in the new variables we find

$$T \left(\dot{\phi} \frac{\partial s}{\partial \phi} + \nabla \dot{\phi} \cdot \frac{\partial s}{\partial \nabla \phi} + \dot{c} \frac{\partial s}{\partial c} + \dot{T} \frac{\partial s}{\partial T} \right) = M \frac{\delta F}{\delta \phi} \frac{\delta F}{\delta \phi} + \nabla \cdot \kappa \nabla T + D \nabla \frac{\delta F}{\delta c} \cdot \nabla \frac{\delta F}{\delta c}, \quad (21)$$

Note, it is usual for $s = -\frac{\partial F}{\partial T}$ to have no dependence on the gradients of ϕ and so $\frac{\partial s}{\partial \nabla \phi} = 0$, but we will assume that this is not the case in general. Now using the phase equation Eq. 1 and

$$\frac{\delta F}{\delta \phi} = \frac{\delta E}{\delta \phi} - T \left(\frac{\partial s}{\partial \phi} - \nabla \cdot \frac{\partial s}{\partial \nabla \phi} \right) \quad (22)$$

where all derivatives are in ϕ, c, T space, we have

$$\begin{aligned} T \frac{\partial s}{\partial T} \dot{T} &= \nabla \cdot \kappa \nabla T - \left(T \frac{\partial s}{\partial \phi} + \frac{\delta F}{\delta \phi} \right) \dot{\phi} - T \frac{\partial s}{\partial \nabla \phi} \cdot \nabla \dot{\phi} - T \frac{\partial s}{\partial c} \dot{c} + D \nabla \frac{\delta F}{\delta c} \cdot \nabla \frac{\delta F}{\delta c} \\ &= \nabla \cdot \kappa \nabla T - \frac{\delta E}{\delta \phi} \dot{\phi} - \nabla \cdot \left(T \frac{\partial s}{\partial \nabla \phi} \right) \dot{\phi} - T \frac{\partial s}{\partial \nabla \phi} \cdot \nabla \dot{\phi} - T \frac{\partial s}{\partial c} \dot{c} + D \nabla \frac{\delta F}{\delta c} \cdot \nabla \frac{\delta F}{\delta c} \\ &= \nabla \cdot \kappa \nabla T - \frac{\delta E}{\delta \phi} \dot{\phi} - \nabla \cdot \left(T \frac{\partial s}{\partial \nabla \phi} \dot{\phi} \right) - T \frac{\partial s}{\partial c} \dot{c} + D \nabla \frac{\delta F}{\delta c} \cdot \nabla \frac{\delta F}{\delta c}. \end{aligned} \quad (23)$$

Now using vector manipulation and c equation to write

$$D \nabla \frac{\delta F}{\delta c} \cdot \nabla \frac{\delta F}{\delta c} \equiv \nabla \cdot \left(D \frac{\delta F}{\delta c} \nabla \frac{\delta F}{\delta c} \right) - \frac{\delta F}{\delta c} \nabla \cdot D \frac{\delta F}{\delta c} = \nabla \cdot \left(D \frac{\delta F}{\delta c} \frac{\delta F}{\delta c} \right) - \frac{\delta F}{\delta c} \dot{c} \quad (24)$$

together with definitions

$$C(\phi, c, T) \equiv T \frac{\partial s}{\partial T} \Big|_{\phi, c}, \quad L(\phi, c, T) \equiv - \frac{\delta E}{\delta \phi} \Big|_{c, T}, \quad K(\phi, c, T) \equiv - \frac{\delta E}{\delta c} \Big|_{\phi, T} \quad (25)$$

and heat flux (recall that the last term in Eq. 26 is zero for usual forms of F)

$$\mathbf{q} \equiv -\kappa \nabla T - D \frac{\delta F}{\delta c} \nabla \frac{\delta F}{\delta c} + T \frac{\partial s}{\partial \nabla \phi} \dot{\phi} \quad (26)$$

this becomes the equation for temperature

$$C \dot{T} + \nabla \cdot \mathbf{q} = L \dot{\phi} + K \dot{c}. \quad (27)$$

Now, from the definition of heat capacity at constant pressure and the total entropy, in equilibrium thermodynamics

$$C_p \equiv T \frac{\partial S}{\partial T} \quad (28)$$

we recognise that C is the generalised heat capacity function: formally different from C_p , but identical in practice because of the forms of the free energy typically chosen and the requirement that the interface width tends to zero. Similar arguments apply to the connection of the function $L(\phi, c, T)$ with the constant latent heat, L . It is clear, in comparing Eq. 27 with Eq. 3, that there are terms neglected in the standard phase field treatment- in particular the heating from solute change, K . For practical computation, using Eq.17,

$$\frac{\partial s}{\partial c} = - \frac{\partial}{\partial c} \frac{\delta F}{\delta T}, \quad \frac{\partial s}{\partial T} \equiv - \frac{\partial}{\partial T} \frac{\delta F}{\delta T} \quad (29)$$

and use Eq. 12 for the variational derivatives of entropy.

Multiphase calculations

The significance of the above lies not only in offering an alternative to formulation of the temperature equation but also suggesting a method for generalising to more complex systems— namely multiphase solidification with physically realistic expressions for free energy. Applying the summation convention, the bracket becomes

$$\begin{aligned}
[A, E] = & - \int_{\Omega} M^{ab} \frac{\delta A}{\delta \phi^a} \frac{\delta E}{\delta \phi^b} d^3x + \int_{\Omega} \frac{M^{ab}}{T} \frac{\delta A}{\delta s} \frac{\delta E}{\delta \phi^a} \frac{\delta E}{\delta \phi^b} d^3x \\
& - \int_{\Omega} D \nabla \frac{\delta A}{\delta c} \cdot \nabla \frac{\delta E}{\delta c} d^3x + \int_{\Omega} \frac{D}{T} \frac{\delta A}{\delta s} \nabla \frac{\delta E}{\delta c} \cdot \nabla \frac{\delta E}{\delta c} d^3x, \\
& - \int_{\Omega} \frac{\kappa}{T} \nabla \frac{\delta A}{\delta s} \cdot \nabla \frac{\delta E}{\delta s} d^3x + \int_{\Omega} \frac{\kappa}{T^2} \frac{\delta A}{\delta s} \nabla \frac{\delta E}{\delta s} \cdot \nabla \frac{\delta E}{\delta s} d^3x,
\end{aligned} \tag{30}$$

and the chain rule becomes

$$\dot{A} = \int_{\Omega} \left(\sum_a \frac{\delta A}{\delta \phi^a} \dot{\phi}^a + \frac{\delta A}{\delta c} \dot{c} + \frac{\delta A}{\delta s} \dot{s} \right) d^3x, \tag{31}$$

from which

$$\dot{\phi}^a = -M^{ab} \frac{\delta F}{\delta \phi^b} \tag{32}$$

and the variational equation for c is as before, Eq 2. The temperature equation generalises Eq. 27 to

$$C\dot{T} + \nabla \cdot \mathbf{q} = - \left. \frac{\delta E}{\delta \phi^a} \right|_{c,T} \dot{\phi}^a - \left. \frac{\delta E}{\delta c} \right|_{\phi,T} \dot{c} \tag{33}$$

where,

$$\mathbf{q} \equiv -\kappa \nabla T - D \frac{\delta F}{\delta c} \nabla \frac{\delta F}{\delta c} + T \frac{\partial s}{\partial \nabla \phi^a} \dot{\phi}^a \tag{34}$$

Note that the mobility has become tensorial, i.e. M^{ab} , in the multiphase formulation: this must be a symmetric matrix. The form of M^{ab} used by [5] is equivalent to a Lagrange multiplier times a scalar mobility, but other forms that preserve the connection with single phase and generalise to n -phase systems are proposed in [7].

Neglected terms – a more general bracket

We have already seen that the bracket formulation offers modifications to terms in the temperature equation. A further advantage of the bracket formulation is that, in greater generality, it highlights terms usually neglected in all the dynamical equations. A more general linear form of the dissipation bracket, than Eq. 13, for the set of variables, $X_a = \{\phi_1, \dots, \phi_n, c, s\}$ is

$$\begin{aligned}
[A, F] = & - \int_{\Omega} M^{ab} \frac{\delta A}{\delta X^a} \frac{\delta E}{\delta X^b} d^3x + \int_{\Omega} \frac{M^{ab}}{T} \frac{\delta A}{\delta s} \frac{\delta E}{\delta X^a} \frac{\delta E}{\delta X^b} d^3x \\
& - \int_{\Omega} N^{ab} \nabla \frac{\delta A}{\delta X^a} \cdot \nabla \frac{\delta E}{\delta X^b} d^3x + \int_{\Omega} \frac{N^{ab}}{T} \frac{\delta A}{\delta s} \nabla \frac{\delta E}{\delta X^a} \cdot \nabla \frac{\delta E}{\delta X^b} d^3x,
\end{aligned} \tag{35}$$

where M^{ab} , N^{ab} are 5×5 diffusion coefficients. By comparison with the above, the bracket given in Eq. 13 does not include gradient terms for ϕ or s , as in the terms for c . It also does not include non-gradient terms for c and, perhaps more crucially, the bracket does not have mixed ϕ , s and c terms. In general, for near equilibrium, these terms must be included unless there is a physical reason opposed to doing so – such as the conservation of c or the time scales of the phenomena is too rapid. Even so there may remain combinations that offer relevant modification to current models.

Summary

We have introduced the mechanics of the dissipative bracket into phase field modelling. The bracket works analogously to the Poisson bracket of classical mechanics and reproduces the standard phase and multi-phase field equations. It also derives the temperature equation directly from the free energy functional, the only extra term required being the thermal conductivity. The resulting thermal equation not only includes a generalised heat capacity and latent heat but also a heat source due to solute concentration changes analogous to phase change. This is a new term currently neglected by standard models. Having established the method for single phase systems the generalisation to multi-phase alloys is shown to be straightforward. The form of the bracket used to reproduce the dynamical equations is not the most general for near equilibrium systems. A more general form is given, suggesting other significant terms are currently overlooked.

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